

# Bulletin of the Agricultural Chemical Society of Japan.

## ABSTRACTS

from

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(Pages refer to the Japanese originals of this volume unless otherwise noticed)

#### Formation of $\beta$ -Hydroxy-pyridine Derivatives from Hexoses and $\text{NH}_3$ -salts. [I].

(pp. 629~633)

By Kiyosi Aso.

(Agricult. Chem. Lab., Tokyo Imp. Univ.; Received June 29, 1939.)

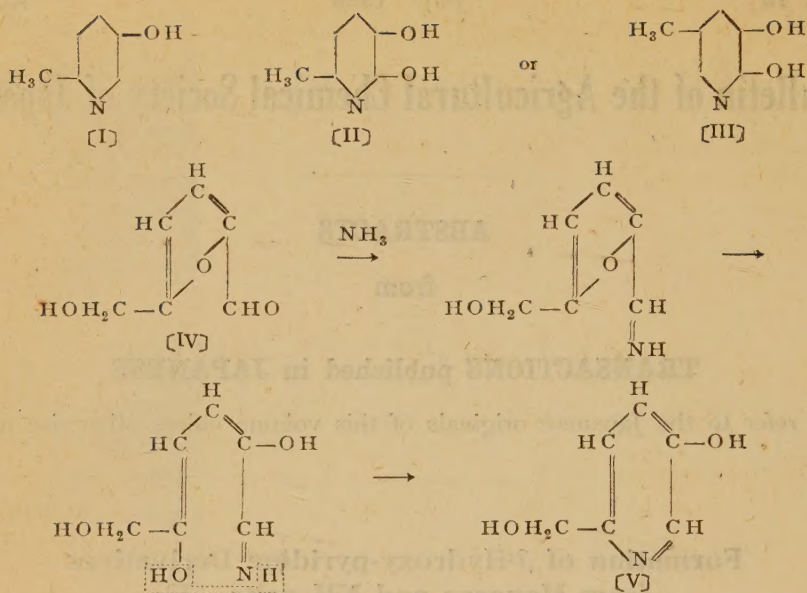
By heating the water solution of glucose or sucrose with  $\text{NH}_3$ -salts in an autoclave, the author obtained 3 different bases, which melt respectively at  $124\sim 125^\circ$ ,  $166\sim 167^\circ$  and  $201\sim 202^\circ$ . Each base gives a blue colour with Folin-Denis phenol reagent but no colour with 2, 6-dichloroquinonechloroimide (Gibbs' reaction).

The base of m.p.  $166\sim 167^\circ$   $\text{C}_6\text{H}_7\text{NO}$  crystallises in colourless prisms, giving a red colour with  $\text{FeCl}_3$  and its picrate forms yellow prisms, melting at  $203\sim 204^\circ$ . This base was identified as 2-methyl-5-hydroxy-pyridine [I] since the free base as well as the picrate did not show depressed melting points on mixed tests with the corresponding authentic specimens.

The base of m.p.  $201\sim 202^\circ$  is obtained in silky crystals (formula:  $\text{C}_6\text{H}_7\text{NO}_2$ ) and its water solution is neutral and gives a deep blue colour with  $\text{FeCl}_3$  and does not form a picrate. The base has properties closely resembling 2- or 3-methyl-5, 6-dihydroxy-pyridine ([II] or [III]) synthesised by Feist. Although it is not yet proved by means of the mixed melting point, it may probably be the same as [II].

The base of m.p.  $124\sim 125^\circ$  is separated from ligroin-alcohol in colourless scaly plates (formula  $\text{C}_6\text{H}_7\text{NO}_2$ ), and its water solution is neutral and gives a reddish brown colour with  $\text{FeCl}_3$ , and its picrate is obtained in yellow prisms melting at  $182\sim 183^\circ$ . Although its investigation is now being continued, the base may be perhaps 2-hydroxymethyl-5-hydroxy-pyridine [IV], which may be derived from hydroxymethyl-furfural [V] and  $\text{NH}_3$  as next equation.





## Studies on the Vegetable Tannins in Formosa.

(pp. 634~638)

By Yasuyosi OSIMA and Hiroshi IRO.

(Agricultural Chemical Department, Taihoku Imperial University,  
Formosa; Received June 13, 1939.)

### Part 3.\*

The tannin contents were determined by the international official method, and the chemical properties of tannins were studied qualitatively. The results were as follows:

Plant names	Water %	Soluble matter %	Non-tannin %	Tannin %	Classification %
<i>Pithecolobium dulce</i> Benth. (bark)	12.6	35.3	8.7	26.6	catechol
<i>Casuarina equisetifolia</i> Lin. ( " )	8.6	19.2	2.3	16.8	"
<i>Ficus elastica</i> Roxb. ( " )	10.1	19.9	5.6	14.3	"
<i>Bischofia javanica</i> Blume ( " )	12.7	9.4	5.0	4.4	"
<i>Elaeocarpus serratus</i> Linn ( " )	9.4	21.5	3.4	18.1	"
<i>Liquidambar formosana</i> Hance ( " )	8.6	15.5	4.6	10.9	"
<i>Elaeocarpus elliptica</i> Nakai ( " )	8.6	18.0	4.2	13.8	"
<i>Ficus religiosa</i> Line. ( " )	8.6	13.5	4.8	8.7	"
<i>Melaleuca leucadendron</i> Linn. (wood)	8.4	3.5	1.0	2.4	"

The absorption amounts of tannins with hide powder were determined by the method reported in Part 2 of this paper. The results are shown in the following:

Tannins:	pH						
	2	3	4	5	6	7	8
<i>Pithecolobium dulce</i> Benth	45.5	36.8	32.4	33.1	33.5	34.5	34.5
<i>Casuarina equisetifolia</i> Linn.	43.5	29.5	25.2	25.4	26.4	27.1	27.8
<i>Ficus elastica</i> Roxb.	43.4	27.9	23.6	21.6	22.6	23.6	24.3

\* Bull. Agr. Chem. Soc. Japan, Vol. 15, 19, 39 (1939).

#### Part 4.

By Yasuyosi OSIMA.

A new catechin has been isolated from the bark of *Casuarina equisetifolia* Linn., named Mokumao in Formosa. It has been shown to be a stereoisomer of the gallo-catechin isolated from tea leaves (Bull. Agr. Chem. Soc. Japan, Vol. 12, No. 8, 1, 1936). This new substance was named "casuarin".

The chloroform solution obtained during the preparation of tannin (B) (Bull. Agr. Chem. Soc. Japan, Vol. 15, 39, 1939) was shaken with water and the water solution was concentrated under diminished pressure and cooled in an ice box. Then the casuarin had crystallised out and it was recrystallised from water. The principal properties are briefly shown in the following:

Physico-chemical properties		Colour reactions:	
m.p.	182°	FeCl <sub>3</sub>	blue-green
[ $\alpha$ ] <sub>D</sub> in aceton-water (1:1)	+19.7	Gelatin	no ppt.
in alcohol	9	Lime water	purple
m.p. of hexacetate	127~128°	HCl-Formalin	White ppt.
[ $\alpha$ ] <sub>D</sub> in aceton "	+34.3	Bromin water	Yellow ppt.
m.p. of penta-methylether	156~158°	KCN	red
[ $\alpha$ ] <sub>D</sub> in acetone	+29.2	Pinewood-HCl	red

The reduction product with metallic sodium was identical with hexamethoxy-diphenyl-propan from gallo-catechin and with a synthetic specimen (loc. cit.). From these results, casuarin has been proved to have the same structure as gallo-catechin, but it is a stereoisomer and corresponds to *d*-form while gallo-catechin from tea is of *l*-epi-form.

#### Über die Spiritusfabrikation unter Verwendung von Dextrinvergärenden Hefen.

(pp. 639~644)

Von Shinji DOI.

(Aus der Agrikult. Chem. Labor., Kaiserl. Univ. zu Tokio;

Received June 7, 1939.)



## Isolation of Four Kinds of Isoflavon from Soya Bean.

(pp. 645~652)

By Koji OKANO and Iwao BEPPU.

(The Central Laboratory of the South Manchurian Railway Co.;

Received June 29, 1939.)

We obtained the following isoflavons from the byproduct of the alcohol extraction of soya bean :—

(1) 8-methyl-5, 4'-dioxylisoflavon, mp. 318°C, white needle, named Tatoin.

(2) 8-methyl-5, 7, 4'-trioxyisoflavon, mp. 298°C, slightly yellow needle, named Methylgenistein.

(3) A glucoside of 8-methyl-5, 7, 2'-trioxyisoflavon, mp. 255°C, slightly yellow needle, named Methylisogenistin.

(4) A glucoside of 5, 7, 2'-trioxyisoflavon, mp. 265°C, also slightly yellow needle, named Isogenistin.

## A Method for Measuring the Color of Fatty Oil.

(pp. 653~658)

By Dr. Kokichi OSHIMA and Tatsuro SUGAWARA.

(From the Chemical Laboratory of the Hakodate College of

Fisheries, Japan; Received June 5, 1939.)

Three sets of standard colors in sealed glass tubes were employed as follows :—

Symbol and No.		Contents	Unit with Lovibond tintometer			
B (Brown)	1	10/3% $K_2Cr_2O_7$ + 2/3% $CrK(SO_4)_2 \cdot 12H_2O$	Yellow	637.3	Red	24.99
	2	1/2[10/3% $K_2Cr_2O_7$ + 2/3% $CrK(SO_4)_2 \cdot 12H_2O$	"	297.4	"	11.66
	3	1/4[ " ]	"	148.7	"	5.83
	4	1/8[ " ]	"	69.4	"	2.72
	5	1/16[ " ]	"	37.0	"	1.45
	6	1/32[ " ]	"	19.7	"	1.00
	7	1/64[ " ]	"	8.0	"	0.60
	8	1/128[ " ]	"	3.0	"	0.48
	9	1/256[ " ]	"	1.3	"	0.30
	10	1/512[ " ]	"	0.4	"	0.14
	11	1/1024[ " ]	"	0.25	"	0.08
	12	1/2048[ " ]	"	0.13	"	0.04
	13	1/4096[ " ]	"	0.07	"	0.02
Y (Yellow)	1	8% $K_2CrO_4$	"	175.8		
	2	4% "	"	105.5		
	3	2% "	"	59.8		
	4	1% "	"	37.9		
	5	1/2% "	"	18.0		



"	6	1/4%	"	"	13.0		
"	7	1/8%	"	"	7.8		
"	8	1/16%	"	"	4.8		
"	9	1/32%	"	"	2.6		
"	10	1/64%	"	"	1.4		
"	11	1/128%	"	"	0.69		
"	12	1/256%	"	"	0.40		
"	13	1/512%	"	"	0.22		
R (Red)	1	20%	$\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	"	1.15	Red	17.0
"	2	10%	"	"	0.7	"	10.8
"	3	5%	"	"	0.4	"	6.4
"	4	5/2%	"	"	0.2	"	3.5
"	5	5/4%	"	"	0	"	1.75
"	6	5/8%	"	"	0	"	0.9
"	7	5/16%	"	"	0	"	0.6
"	8	5/32%	"	"	0	"	0.32

A sample of fatty oil is placed in a test tube which is the same size as those of the standard colors and is compared with the standard color tubes in a comparator box. The result of the comparison is expressed by the symbol and number of the standard tube whose color is identical with that of the sample oil.

The colors of the standard solutions do not fade for a long period of time even under direct sunlight.

### On the Stimulant for Cane Sugar Formation in Plants. (III)

(pp. 659~660)

By Tetutarō TADOKORO.

(Biochem. Lab., Faculty of Sci., Hokkaido Imp. Univ.,

Received June 15, 1939.)

### Studies on the Amylo-Process for the Production of Alcohol from Potatoes. (II).

(pp. 661~668)

By Shinji Dor.

(Agricultural Chemical Laboratory, Tokyo Imperial University;

Received June 7, 1939.)



## Statistic Studies of Soils. (VIII).

(pp. 669~684)

By Dr. MISU-Hideo and RIHOKI.

(Agricultural Experiment Station, Government General of Tyōsen;

Received June 2, 1939.)

## Synthesis of Iso-ochracin.

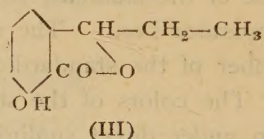
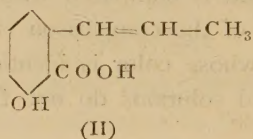
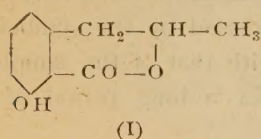
The Metabolic Products of *Aspergillus Ochraceus*. Part III.

(pp. 685~689)

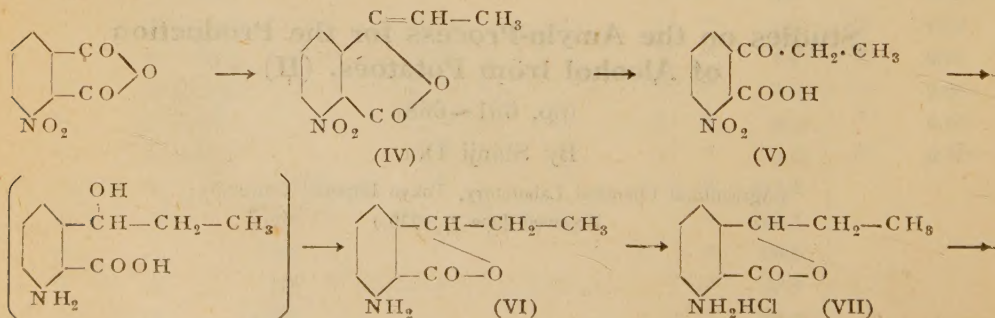
By Teiichi TAMURA.

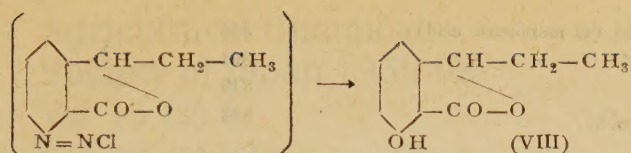
(Agricult. Chem. Lab., Tokyo Imp. Univ; Received June 29, 1939.)

It has been shown by T. Yabuta and Y. Sumiki that ochracin (I), a new metabolic product of *Aspergillus ochraceus*, yielded melleic acid (II) on kalifusion under a mild condition, from which, by treatment with sulphuric acid, iso-ochracin (III) was prepared.

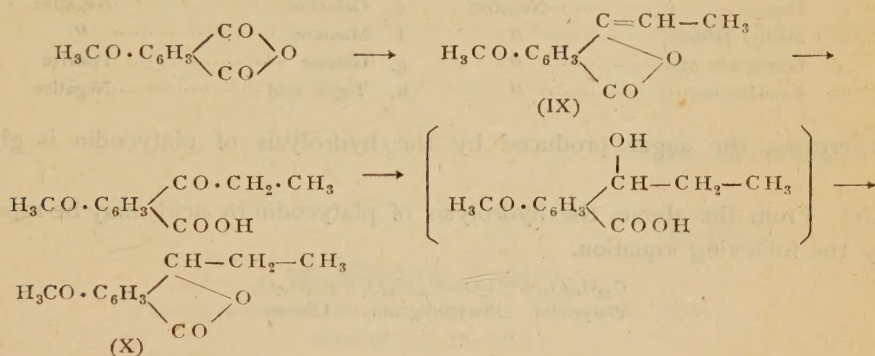


The author has now confirmed by the following synthesis that iso-ochracin is identical with 7-oxy-ethylphthalide substantiating the conclusion of Yabuta and Sumiki. According to Gabriel's method for preparing benzal-phthalides, 3-nitro-phthalic anhydride is heated with propionic anhydride and anhydrous sodium propionate to prepare 7-nitro-ethyliden-phthalide (IV). IV is dissolved in warm dilute alkali and 6-nitro-2-propionyl-benzoic acid (V) is obtained. By the reduction of V with a large excess of sodium amalgam, 2<sup>1</sup>-oxy-2-propyl-6-amino-benzoic acid is obtained, which, when neutralized with hydrochloric acid, gives 7-amino-ethylphthalide (VI). From (VI) by treating with hydrochloric acid in alcoholic solution, 7-amino-ethylphthalide chlorohydrate (VII) is obtained. This substance is diazotized and led to 7-oxy-ethylphthalide (VIII), identical in all respects with iso-ochracin.





In the next experiment, synthesis of methyl-iso-ochracin was attempted, starting from 3-methoxy-phthalic anhydride instead of from 3-nitrophthalic anhydride. According to the same method above described, 7- or 4-methoxy-ethyliden phthalide (IX) is prepared. This substance, on reduction with sodium-amalgam and on subsequent acidification with sulphuric acid, gives 7- or 4-methoxy-ethyl-phthalide (X), m.p. 58°.



On the contrary, the methylated product of iso-ochracin which is prepared by its methylation with diazomethane, dimethylsulfate or methyl iodide is obtained only as an oily matter.

From this experiment, the resulting crystal (X) is recognized as 4-methoxy ethylphthalide to the best of my belief, although the choice between the 4- or 7-isomer is not yet clearly decided.

### Chemical Studies on the Kikyo-root. (Report VII).

The molecular weight and the hydrolysis of platycodin.

(pp. 690~695)

By M. TSUJIMOTO and T. MATSUMOTO.

(Agr. Chem. Laboratory, Kyushu Imp. Univ., and Agr. Chem. Laboratory, Imp. College of Agr. and Forestry; Received June 30, 1939)

#### Conclusions

(1) The result of the elementary analysis of platycodin was as follows:

Found	C% = 60.11	H% = 8.06
Calc. for $\text{C}_{43}\text{H}_{68}\text{O}_{17}$	" = 59.72	" = 8.06

(2) The molecular weight of platycodin was determined by the method of titration and Barger's method.



Titration method (as monobasic acid)	836
Barger's method	801
Mean	819
Calc. for $C_{42}H_{68}O_{17}$	844

- (3) The following two processes of hydrolysis of platycodin were examined.
- By boiling it with 5%-alcoholic HCl the hydrolysis was completed in 20 hours.
  - By boiling it with 5%-alcoholic  $H_2SO_4$  the hydrolysis was completed in 100 hours.
- (4) The qualitative determination of sugar in the syrup.

a. Pentose.....	Negative	e. Galactose.....	Negative
b. Methyl pentose .....	"	f. Mannose .....	"
c. Glucuronic acid .....	"	g. Glucose .....	Positive
d. Keto-hexose.....	"	h. Tiglic acid .....	Negative

Therefore, the sugar produced by the hydrolysis of platycodin is glucose only.

- (5) From the above, the hydrolysis of platycodin by acids may be represented by the following equation.

